

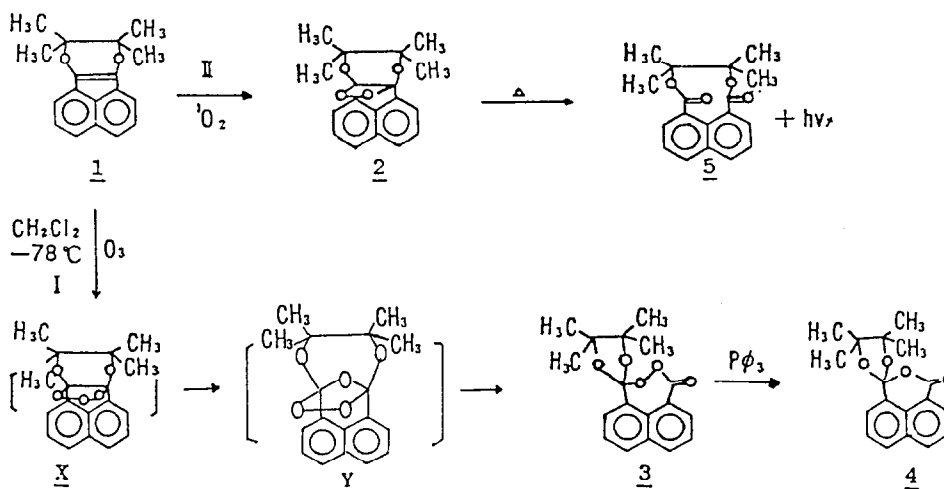
OZONATION AND CHEMILUMINESCENCE OF 8,8,9,9-TETRAMETHYLACENAPHTHO-[1,2-b]-1,4-DIOXIN.
 EVIDENCE FOR DUAL REACTION PATHWAYS.

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Summary: Chemiluminescence and 90% of a highly unusual spiro peroxide 3 were obtained in the ozonation of compound 1 in dichloromethane or methanol.

Ozone induced chemiluminescence of organic compounds has received considerable attention.¹ Nearly all of the gas phase reactions are chemiluminescent.² A large number of organic chemicals both in solution and solid state show chemiluminescence, when ozone is bubbling through.³ Prior attempts to understand this phenomenon have not been successful.⁴ We report herein our studies on the ozonation of the title compound 1.⁵ The results reveal that the reaction is chemiluminescent. The major adduct is a rearranged ozonide 3, which is not chemiluminescent. The responsible light source is coming from the side reaction adduct, the well-known dioxetane type compound 2.⁶ The overall reactions are summarized in the scheme:



Compound 1 was ozonized in dichloromethane or methanol at $-78^\circ C$. The discharge of the scarlet color signified the finish of the reaction. On warming up to ice temperature, no chemiluminescence was observed. In connection with this study, the 1H NMR of the major product was invariant over this temperature range. A skyblue chemiluminescence, however, was noticed

upon heating above room temperature. The higher the temperature, the brighter and shorter duration of the chemiluminescence.

The ozonized adducts were separated by silica-gel, thin layer chromatography, eluted at 0°C with CHCl₃: n-hexane 1:1, yielding less than 2% of the chemiluminescent adduct ($R_f=0.75$), which is consistent with that prepared by the controlled singlet oxygen condition.⁷ Fig.1 shows the ¹H NMR spectra of the ozonized chemiluminescent species 2 contaminated with a small amount of decomposed compound 5 (A) and diester 5 after complete decomposition (B). Recrystallization of the decomposed product with methanol gave the light yellow needle crystals 5.

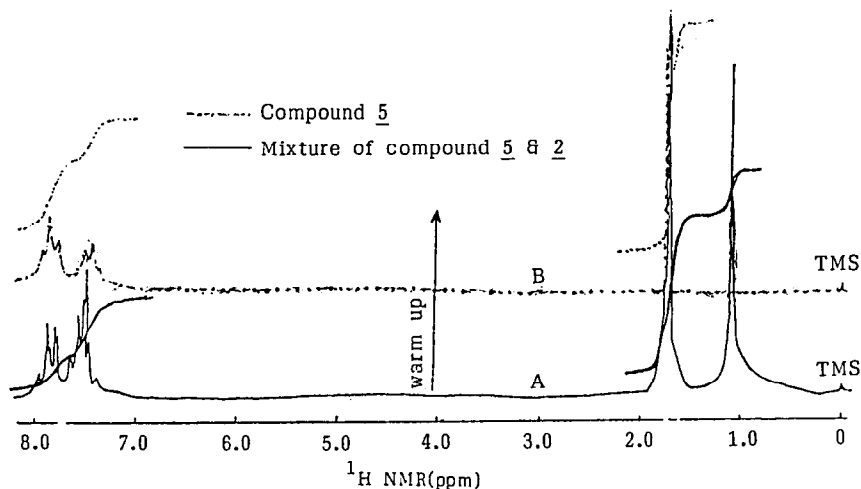


Fig. 1. The ¹H NMR of the chemiluminescent species before and after decomposition.

The chemiluminescence spectrum peaking at 350 nm is consistent with that of the photofluorescence of diester 5. It further confirms the chemiluminescence source. The thermoparameters of 2 are listed in Table 1, which are in agreement with other dioxetanes.⁸

Table 1, Experimental Thermo-parameters of 2

T(K)	k(sec ⁻¹)#	E _a *	log A*
318	0.000243		
323	0.000392		
333	0.000961	19.7 Kcal/mole	10.3
343	0.003106		
353	0.009382		

The chemiluminescence decay monitored at 350nm in cyclohexane

* Based on the equation $k=A^{-E_a/RT}$

The ozonized product was recovered in 90% yield by TLC and then recrystallized to yield white crystals. The physical data (Table 2) and single crystal x-ray diffraction analysis⁹ elucidate the structure of the non-chemiluminescent ozonide adduct as a highly unusual spiro peroxide 3. That

reaction of 3 with triphenylphosphine¹⁰ in benzene gave compound 4, further confirms the structure 3.

Table 2. The Physical Data of Compound 3, 4 and 5

Compound	<u>3</u>	<u>4</u>	<u>5</u>
M.P.(°C)	134	170	202
¹ H NMR(ppm) Alkyl H	1.47(s), 1.60(s)	1.39(s), 1.63(s)	1.75(s)
¹³ C NMR (ppm)	24.78 126.03 87.89 126.21 136.23 128.37 132.01 136.41 172.80	25.05 87.13 125.09 127.21 130.32 127.42 130.08 134.41 163.30	26.02 88.71 125.10 132.31 129.83 169.98
IR (cm ⁻¹)	850 1150 1210 1320 1720	840 1210 1320 1720	1700 1730
UV-Vis λ(nm) ε	230 ⁴ 3x10 ⁴ 310 ⁴ 1.2x10 ⁴	225 ⁴ 3.5x10 ⁴ 300 ³ 8.0x10 ³	220 ⁴ 3x10 ⁴ 300 ⁴ 1x10 ⁴
MS Fragment Rel. Int.	314 270 190 172 126 84 6.3 3.5 18.8 85.9 40.6 100	298 254 240 198 182 172 154 126 2.3 21.8 2.6 1.3 14.1 100 41.1 30.8	298 254 240 216 198 182 172 154 126 21.9 1.8 39.2 1.6 13.5 100 9.2 18.6 4.7
Elements Micro. Anal.	Calc. 68.79%(C) 5.73%(H) Found. 68.90%(C) 5.76%(H)	Calc. 72.48%(C) 6.04%(H) Found. 72.56%(C) 6.08%(H)	—————
Crystal Type	needle, light yellow	Granule, white	Granule, white

Extensive mechanistic investigation of the liquid-phase reaction of ozone with olefins has established the Criegee zwitterion mechanism¹¹ through the identification of many of the reaction intermediates. Attempts to obtain proofs for the existence of moloozonide x and ozonide y in the ozonation of the title compound 1 have not been successful. However, the rearranged adduct 3 in 90% yield is understandable in terms of these intermediates. No chemiluminescence was observed in controlled experiments involving ozonation of the solvents (CH₂Cl₂ or MeOH) which rules out the solvent contribution to the ozone-induced chemiluminescences.¹² The failure to isolate the epoxide adduct of 1 argues against the mechanism proposed by Janzen et al.¹³ for the chemiluminescent reaction of ozone with 10,10'-dimethyl-9,9'-biacridylidene. Then, how is 2 formed during ozonation? Fonder and Hudson¹⁴ reported that 10 to 20 percent of molecular singlet oxygen is produced by passing a stream of oxygen through an electric discharge. Corey and Taylor¹⁵ were the first to recognize that this source of singlet oxygen might be used to oxygenate organic substrates. Our results, summarized in the above scheme, seem to support the idea of dual reaction pathways during the ozonation of the title compound 1.

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9. Compound **3** single crystal was analyzed by CAD4 Kappa Axis Single Crystal XRD located in the Department of Chemistry, National Taiwan University. Possible Space Group: $P_{21/c}$ with lattice constants $a=10.1559(19)$, $b=13.5535(32)$, $c=11.8031(25)$ and $\beta=103.92(2)$; Data Collection: Mo radiation source, room temperature, $2^\circ-60^\circ\text{C}$ 2θ range, $2(0.7+0.35\tan\theta)$ (5) scan parameter 4965 ($2016>3\sigma$). ; Structure Analysis Procedure: using direct method to determine the model of structure and then least square method to refine the position of atoms until $R_1=6.27\%$, $R_2=4.00\%$.
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